Lawrence Livermore National Laboratory

Chemical Kinetic Research on HCCI & Diesel Fuels

William J. Pitz (PI)
Marco Mehl, Charles K. Westbrook
Lawrence Livermore National Laboratory
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Project ID # ACE013

DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation

Washington, DC

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Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

LLNL-PRES-628234

Overview

Timeline

- Project provides fundamental research to support DOE/ industry advanced engine projects
- Project directions and continuation are evaluated annually

Budget

Project funded by DOE/VT:

- FY12: 620K
- FY13: 600K

Barriers

- Increases in engine efficiency and decreases in engine emissions are being inhibited by an inadequate ability to simulate in-cylinder combustion and emission formation processes
  - Chemical kinetic models for fuels are a critical part of engine simulation models

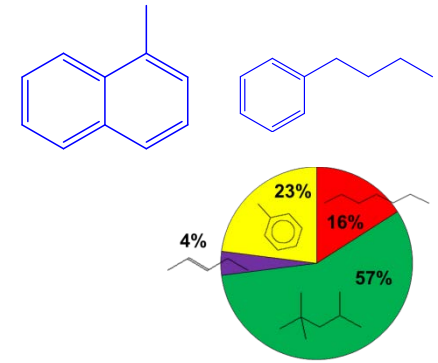
Partners

- Project Lead: LLNL – W. J. Pitz (PI)
- Part of Advanced Engine Combustion (AEC) working group:
- – 15 Industrial partners: auto, engine & energy
- – 5 National Labs & 2 Univ. Consortiums
- Sandia: Provides engine data for validation of detailed chemical kinetic mechanisms
- FACE Working group

Objectives and relevance to DOE objectives

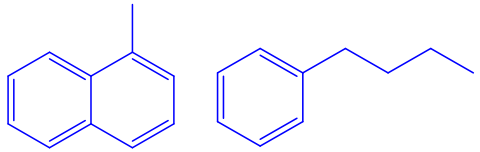
- Objectives:
  - Develop predictive chemical kinetic models for gasoline, diesel and next generation fuels so that simulations can be used to overcome technical barriers to low temperature combustion in engines and needed gains in engine efficiency and reductions in pollutant emissions

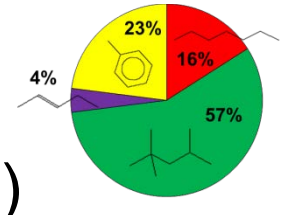
- FY13 Objectives:
  1. Develop detailed chemical kinetic models for larger alkyl aromatics relevant to diesel fuels
  2. Develop more accurate surrogate kinetics models for gasoline-fueled HCCI, including ethanol
  3. Develop improved chemical kinetic models for larger alkyl-cyclohexanes
  4. Develop an improved 2-component surrogate mechanism for diesel to be used for multidimensional CFD simulations

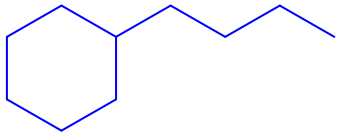


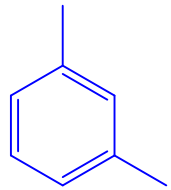
Chemical kinetic milestones

1. Develop detailed chemical kinetic models for larger alkyl aromatics (June, 2013)
2. Develop more accurate surrogate kinetics models for gasoline-fueled HCCI including ethanol (Sept, 2013)
3. Develop improved chemical kinetic models for methyl cyclohexane and a preliminary model for n-butyl cyclohexane (Sept, 2013)
4. Develop an improved 2-component surrogate mechanism for diesel to be used for multidimensional CFD simulations (March, 2013)









Approach

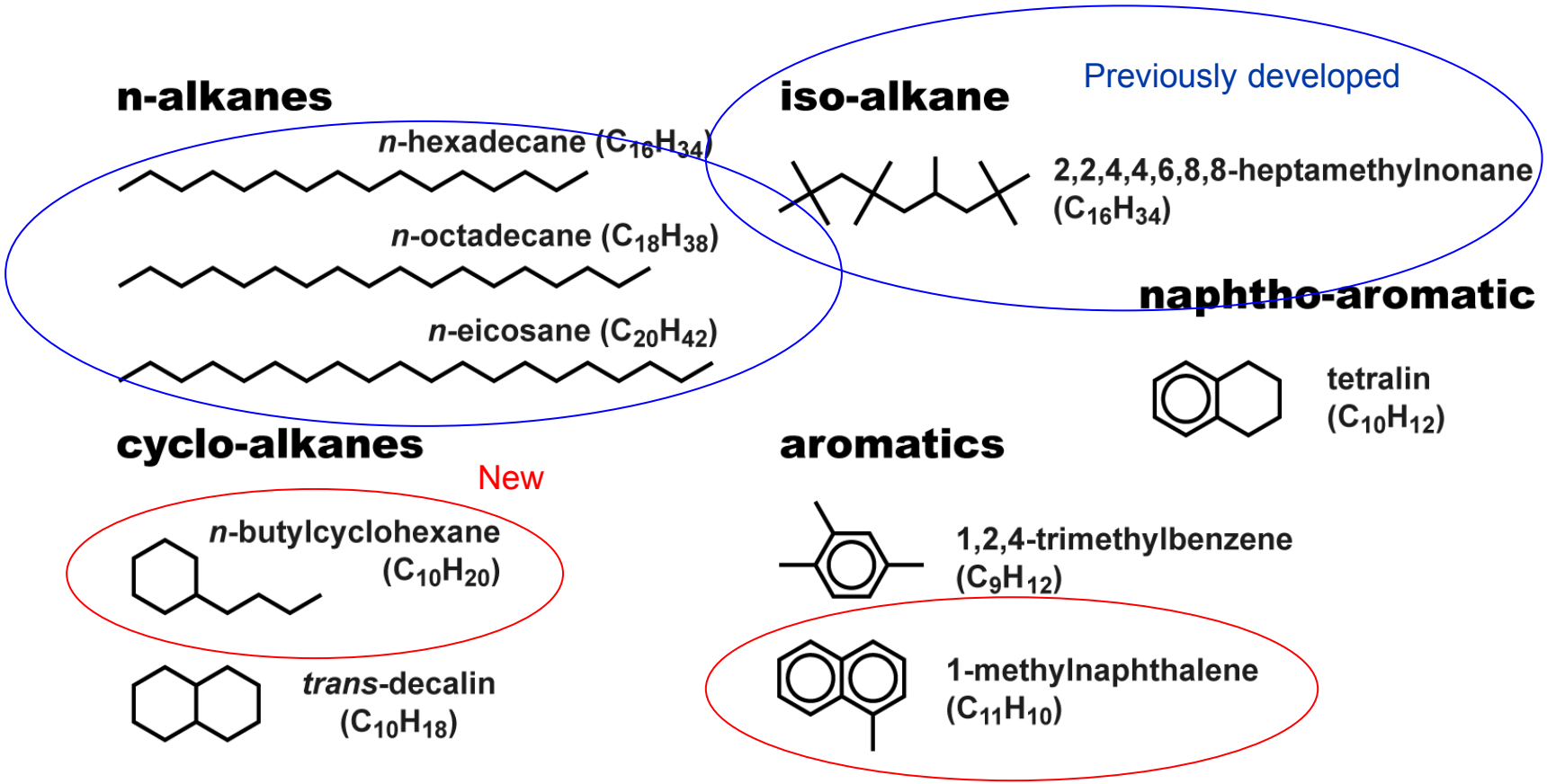
- Develop chemical kinetic reaction models for each individual fuel component of importance for fuel surrogates of gasoline, diesel, and next generation fuels
- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels
  - diesel fuel
  - gasoline (HCCI and/or SI engines)
  - addition of ethanol and other biofuels
- Reduce mechanisms for use in CFD and multizone HCCI engine codes to improve the capability to simulate in-cylinder combustion and emission formation/destruction processes in engines
- Use the resulting models to simulate practical applications in engines, including diesel, HCCI and spark-ignition, as needed
- Iteratively improve models as needed for applications
- Make models available to industry

Collaborations

- Our major current industry collaboration is via the DOE working groups on HCCI and diesel engines
  - All results presented at Advanced Engine Combustion Working group meetings (Industry, National labs, U. of Wisc., U. of Mich., MIT, UC Berkeley)
  - Multiple exchanges of chemical kinetic models with industry
  - Collaboration on gasoline-ethanol engine experiments with Sandia:
    - John Dec on HCCI
    - Magnus Sjöberg on DISI
  - Collaboration with Sibendu Som at Argonne on diesel reacting sprays
- Second interaction is collaboration with many universities
  - Prof. Sung's group, U of Conn., Dr. Sarathy, KAUST, and Prof. Dibble, UC Berkeley on gasoline surrogates
  - Dr. Curran at Nat'l Univ. of Ireland on n-propyl benzene and n-butyl benzene in RCM and shock tube
  - Prof. Reitz, Univ. of Wisc., on development of reduced chemical kinetic models for diesel surrogate components
  - Prof. Lu, U. of Conn. on mechanism reduction
- Participation in other working groups with industrial representation
  - Fuels for Advanced Combustion Engines (FACE) Working group and AVFL-18 (Surrogate fuels for kinetic modeling)
  - Engine combustion network (ECN)

Technical Accomplishment slides:
Diesel components selected for mechanism development in FY13

Components selected from the AVFL-18 Diesel Surrogate palette[1]:



[1] CRC AVFL-18 Working Group. Mueller, C. J., Cannella, W. J., Bruno, T. J., Bunting, B., Dettman, H. D., Franz, J. A., Huber, M. L., Natarajan, M., Pitz, W. J., Ratcliff, M. A. and Wright, K., Energy & Fuels 26(6):3284–3303 (2012).

Fuel component and surrogate models validated by comparison to fundamental experimental data

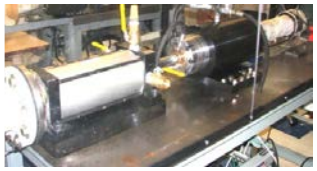
Jet Stirred Reactors

Premixed Laminar Flames

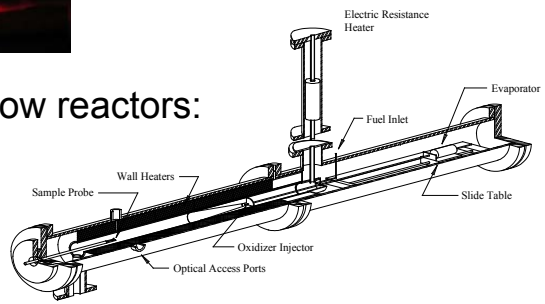
Shock tube

Non Premixed Flames

Rapid Compression Machine



High pressure flow reactors:



Engine Combustion

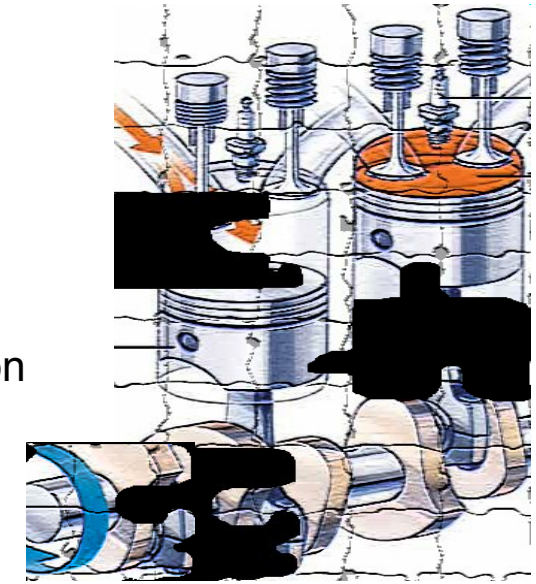
Combustion Parameters

Temperature

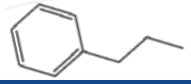
Pressure

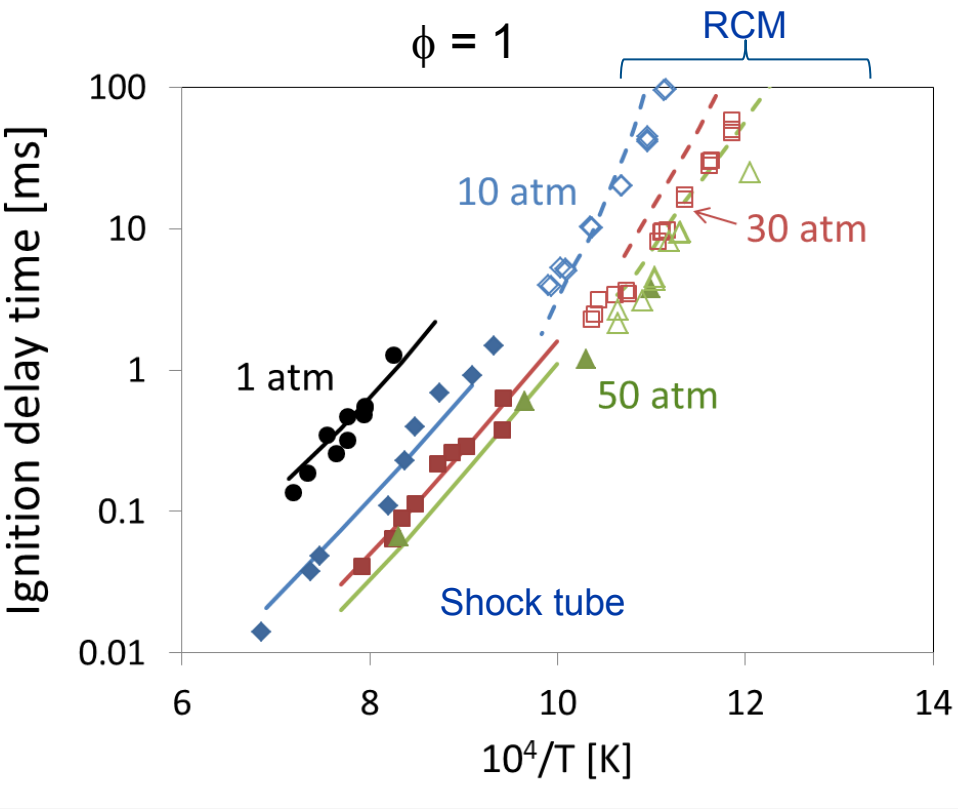
Mixture fraction (air-fuel ratio)

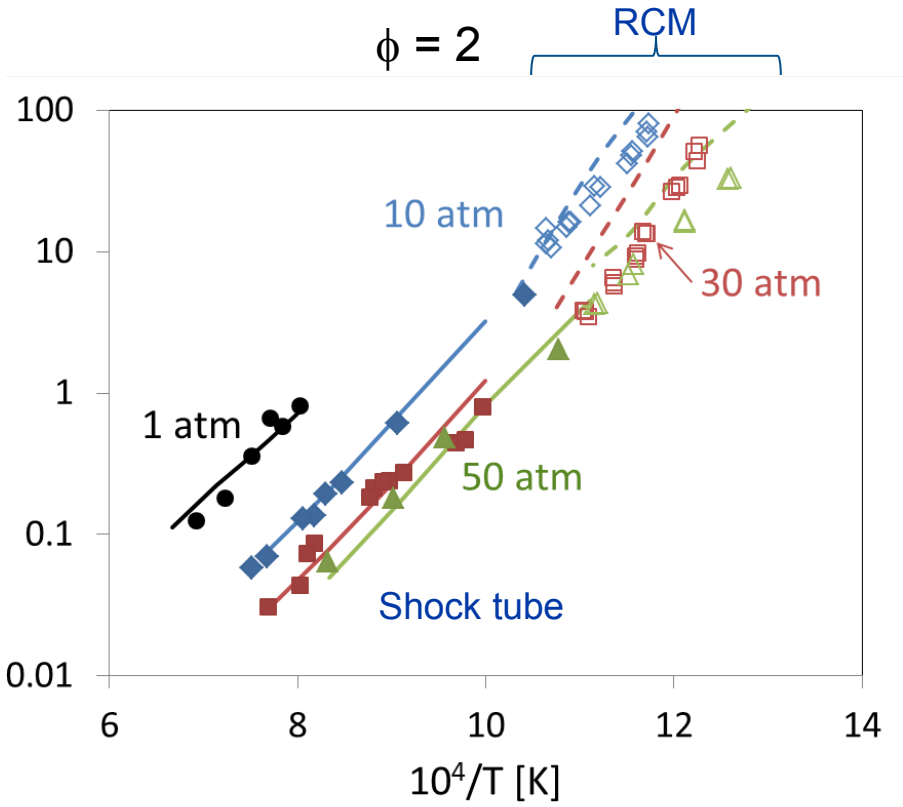
Mixing of fuel and air



Objective 1: Develop detailed chemical kinetic models for larger alkyl aromatics relevant to diesel fuels. N-propyl benzene mechanism simulates well ignition in shock tubes and RCM over a wide range of pressures and temperatures







Shock tube

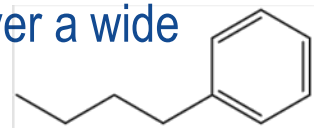
Rapid compression machine (RCM)

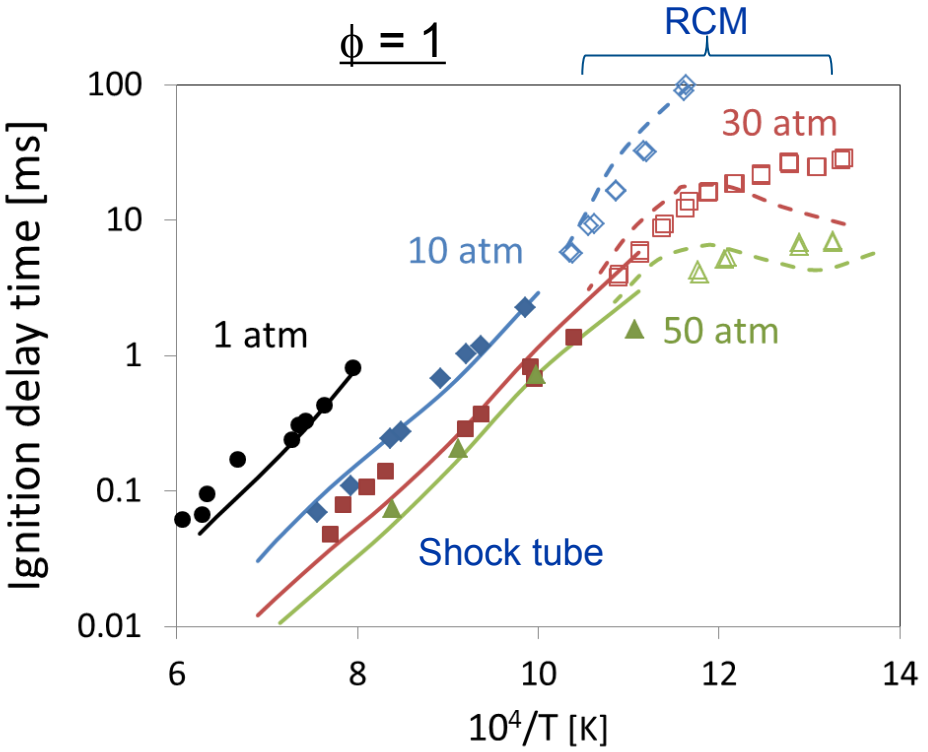
Experiments:
Nakamura and Curran , NUI-Galway, Ireland

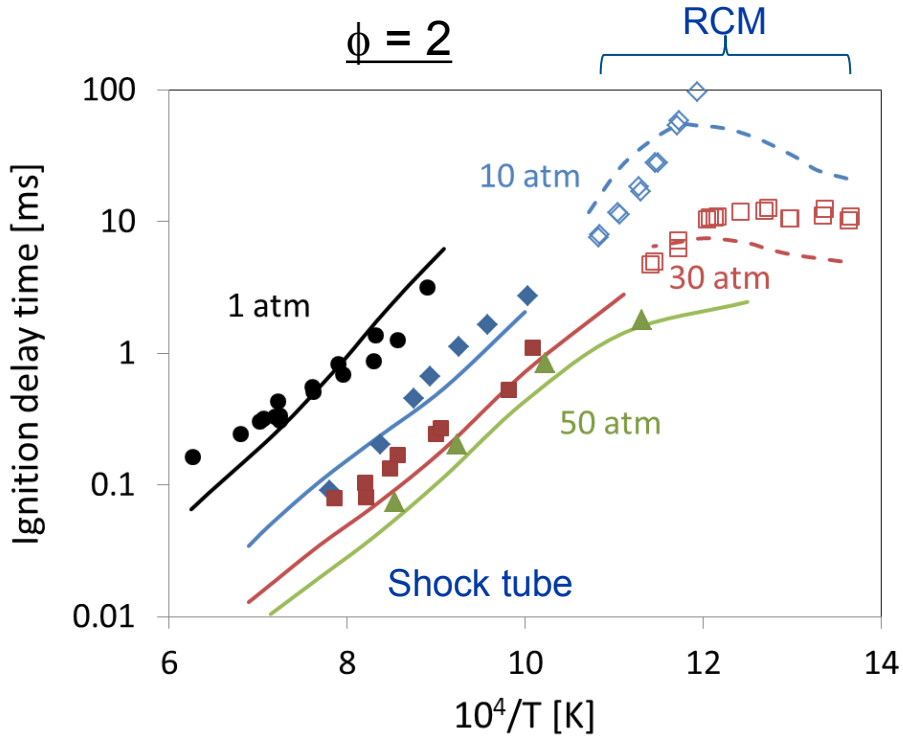
Technical accomplishments

Objective 1: (Continued)

N-butyl benzene mechanism well simulates ignition in shock tubes and RCM over a wide range of pressures and temperatures







Shock tube

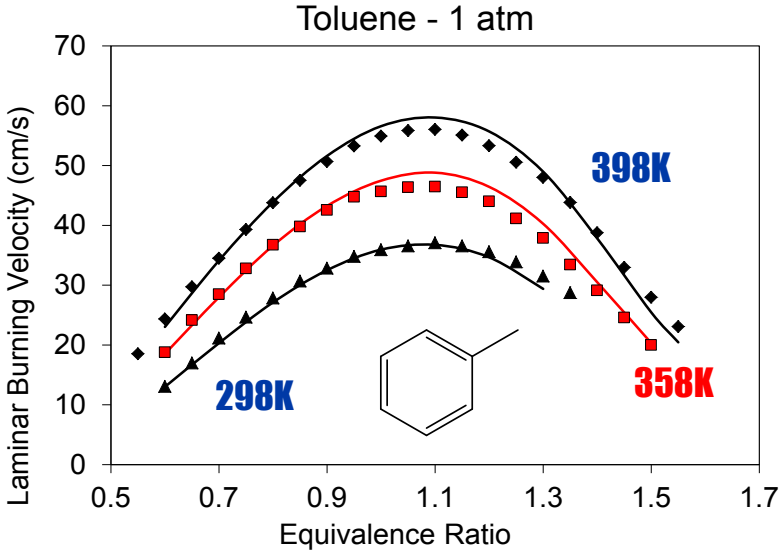
Rapid compression machine (RCM)

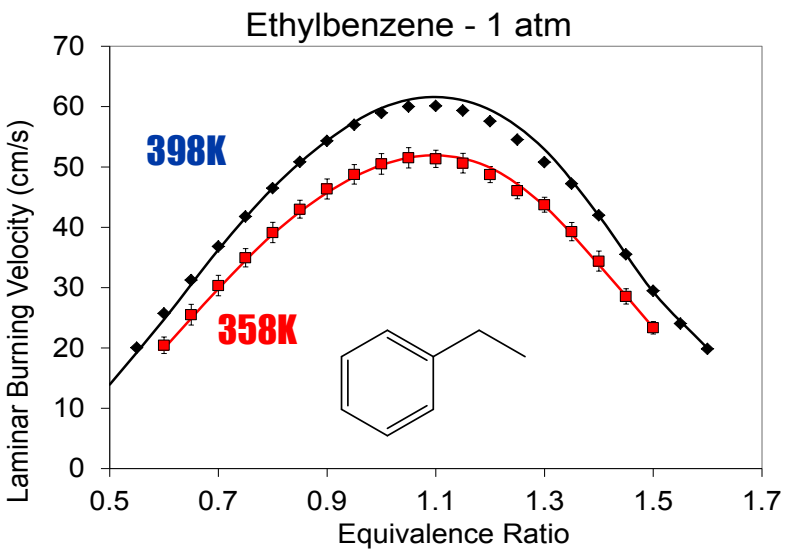
Experiments:

Nakamura and Curran , NUI-Galway, Ireland

Technical accomplishments

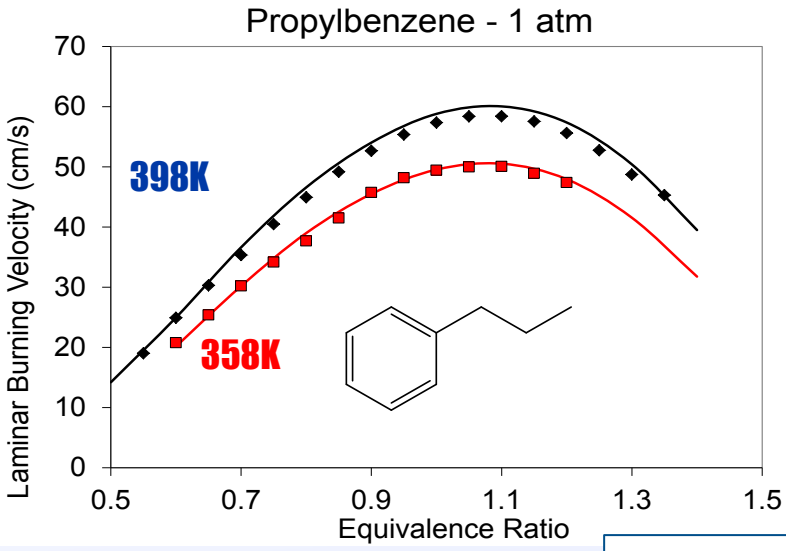
Objective 1: (Continued)
Our alkyl benzene mechanisms perform very well compared to experimental flame speeds

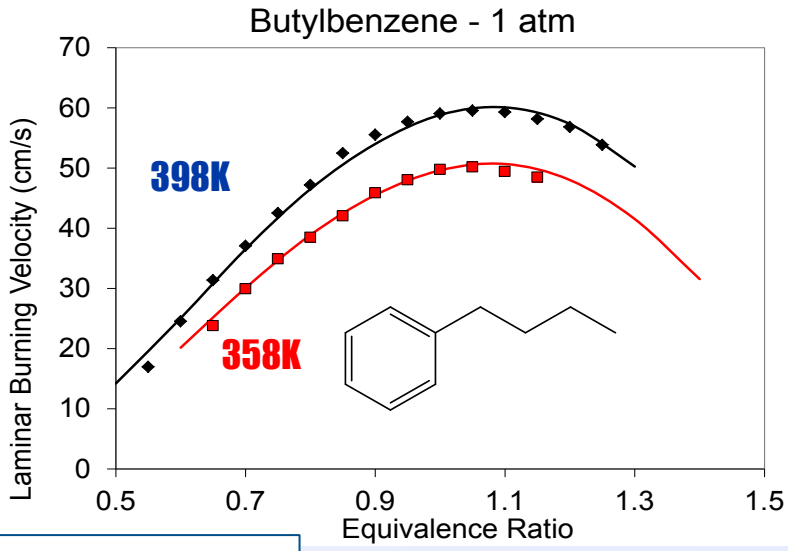




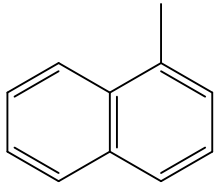
Experiments:

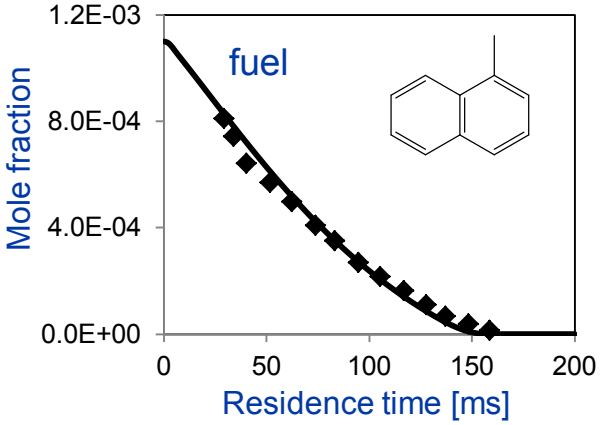
Dirrenberger, Herbinet, et al., U. S. National Combustion Meeting, 2013.

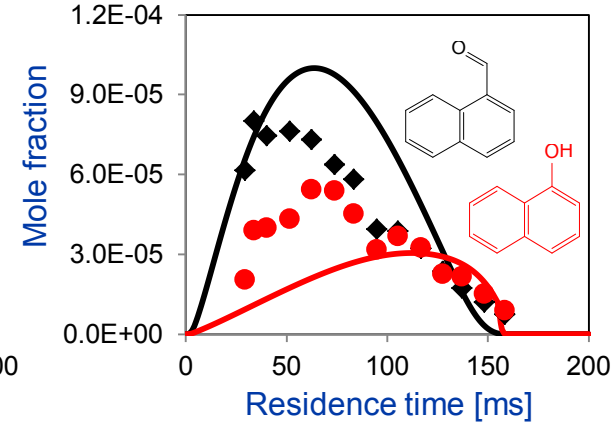


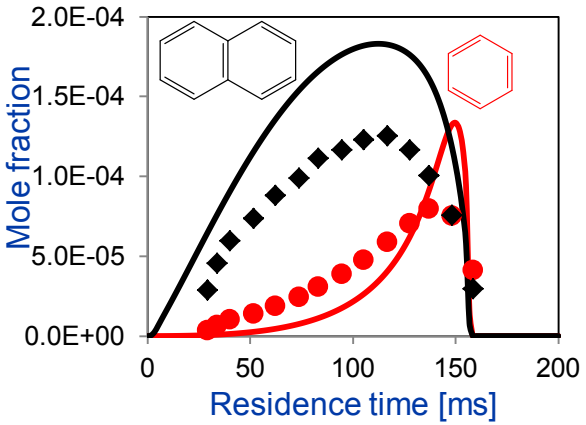


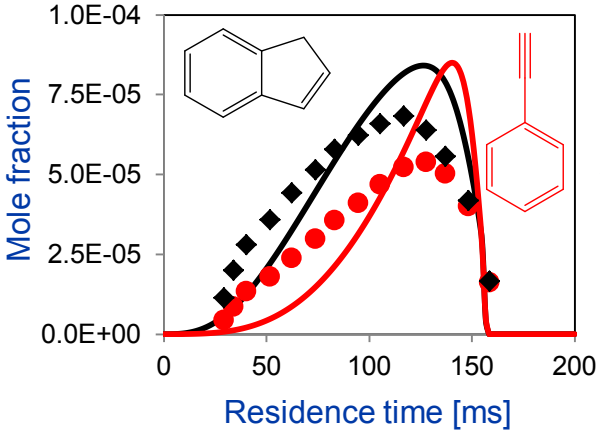
Objective 1: (Continued)
Intermediate species for α-methylnaphthalene oxidation are well predicted in a flow reactor

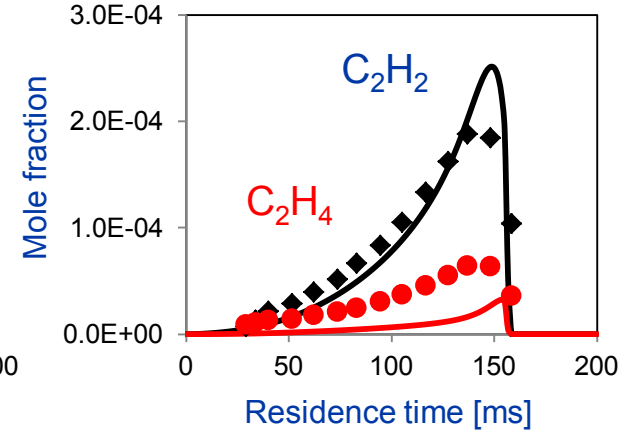


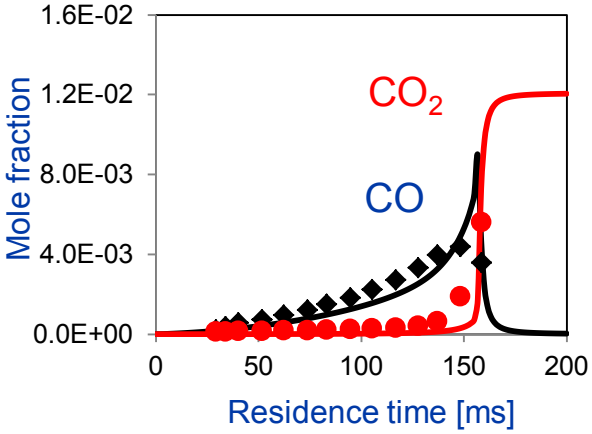


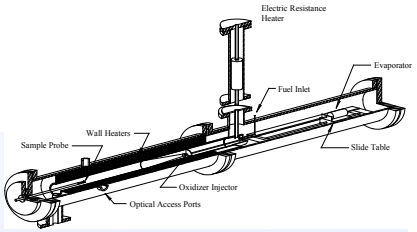






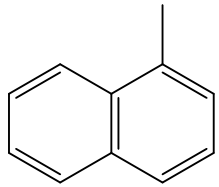


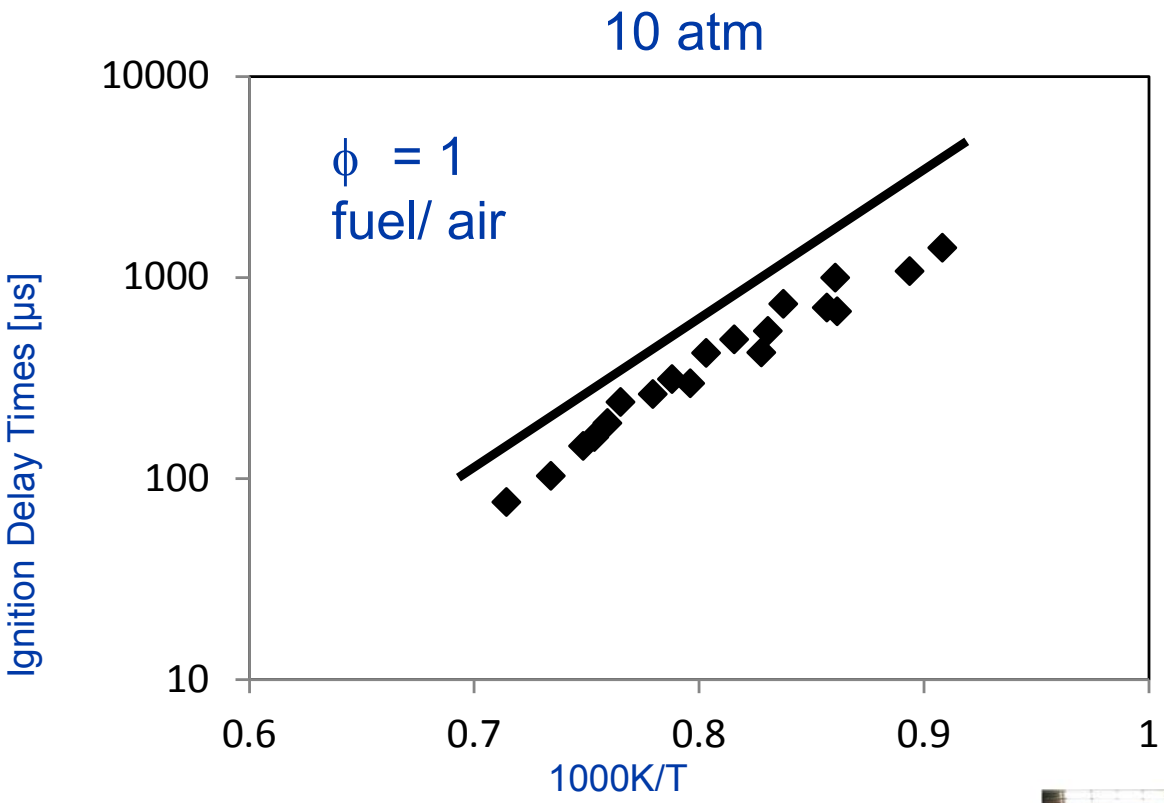




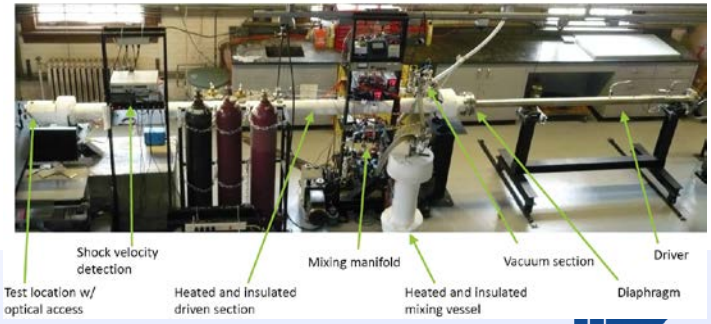
Flow reactor, P = 1 atm, ϕ = 0.5, (Shaddix et. al., 1997)

Objective 1: (Continued)
Ignition delay times for α-methylnaphthalene are reasonable compared to shock tube ignition experiments

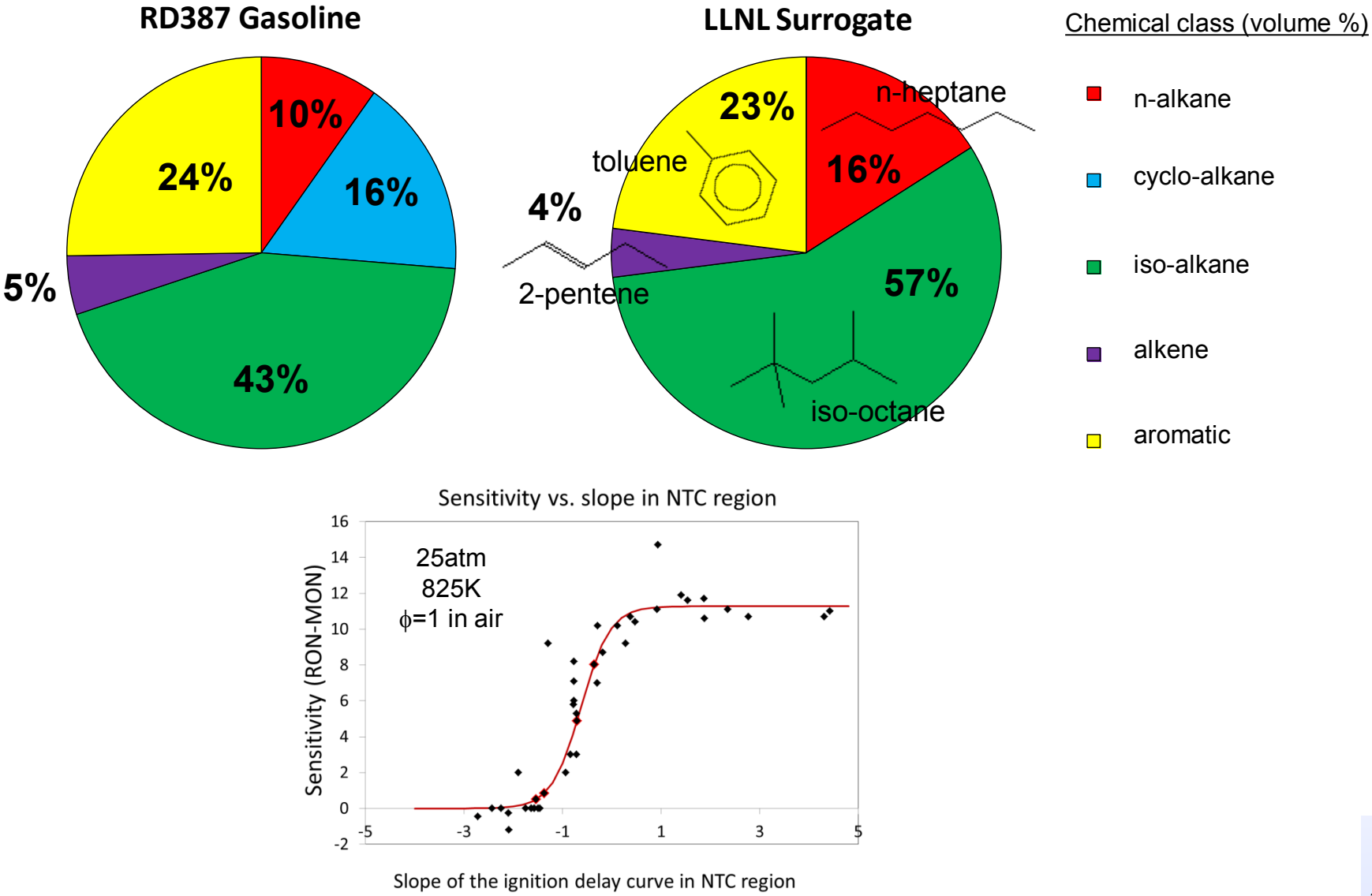




Experiments: Wang and Oehlschlaeger et al., Combust. Flame, 2010



Objective 2: Develop surrogate for gasoline-ethanol mixtures: LLNL 4-component surrogate model for gasoline



Objective 2 (Cont.):
Developed surrogate mixtures for each of the gasoline-ethanol mixtures

Gasoline-ethanol surrogate composition (volume %)

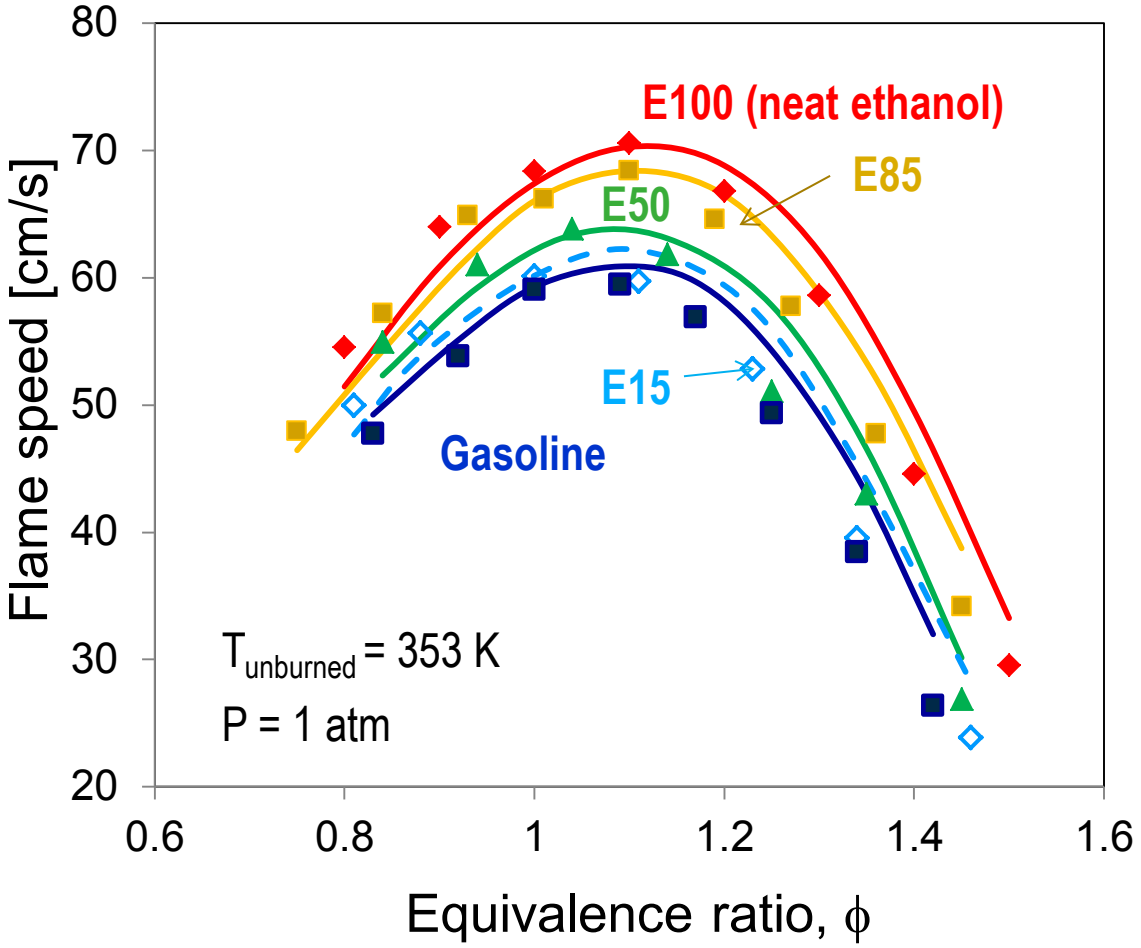
	RD387	E15	E50	E85	E100
iso-octane	57 %	48.4 %	28.5 %	8.55 %	–
n-heptane	16 %	13.6 %	8.0 %	2.40 %	–
toluene	23 %	19.6 %	11.5 %	3.45 %	–
2-pentene	4 %	3.4 %	2.0 %	0.60 %	–
ethanol	–	15.0 %	50.0 %	85.00 %	100 %

Objective 2 (Cont.): Gasoline-ethanol surrogate model with ethanol well simulates laminar flame speed for gasoline-ethanol mixtures

Twin premixed flames

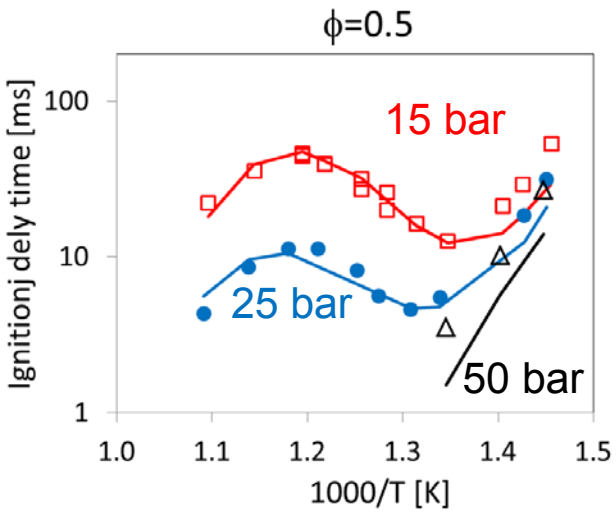
Experiments:
Runhua Zhao, Egolfopoulos, USC

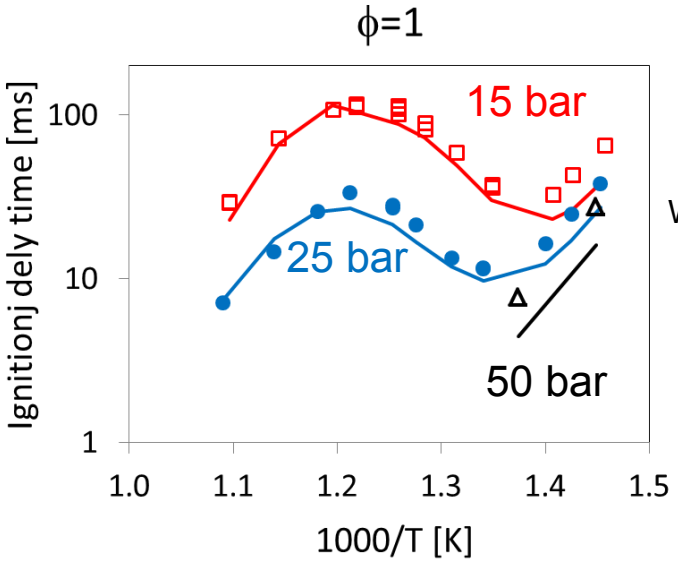
RD387 gasoline-ethanol mixtures:
Supplied by Magnus Sjöberg, SNL



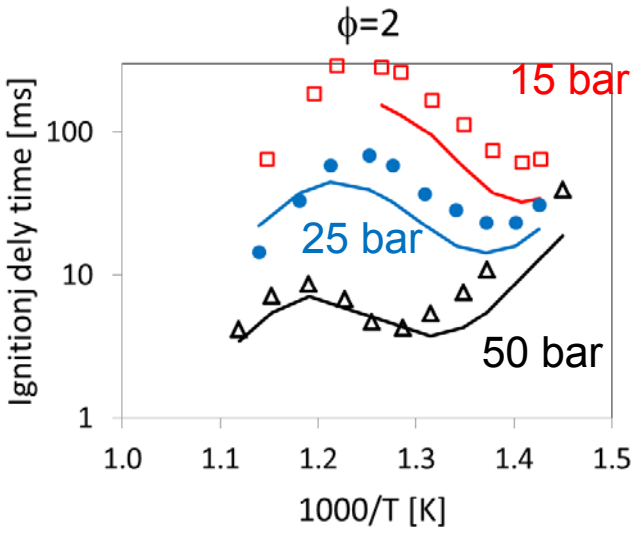
Objective 3: Develop chemical kinetic models for larger alkyl-cyclohexanes.

Improved methylcyclohexane (MCH) model simulates RCM ignition well at 15, 25 and 50 bar

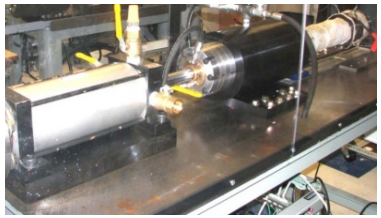




Weber, Pitz, Sung et al., 2013 U.S. National Combustion Meeting



UCONN RCM



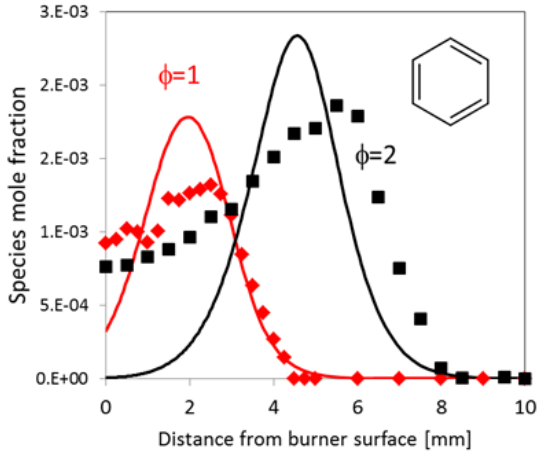
Experiments: Weber and Sung, UCONN

Technical accomplishments

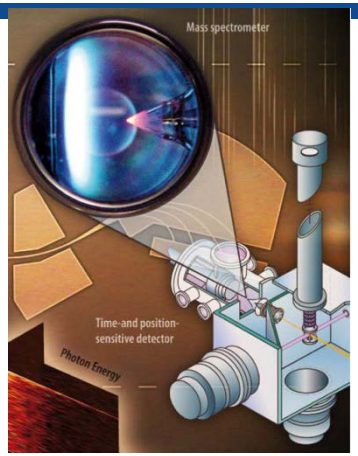
Objective 3 (Cont.)

Updated MCH mechanism satisfies a rigorous set of experimental species profiles in flames

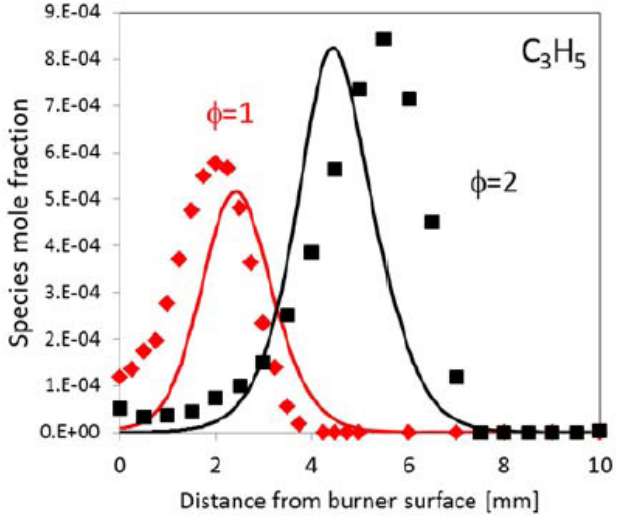
benzene

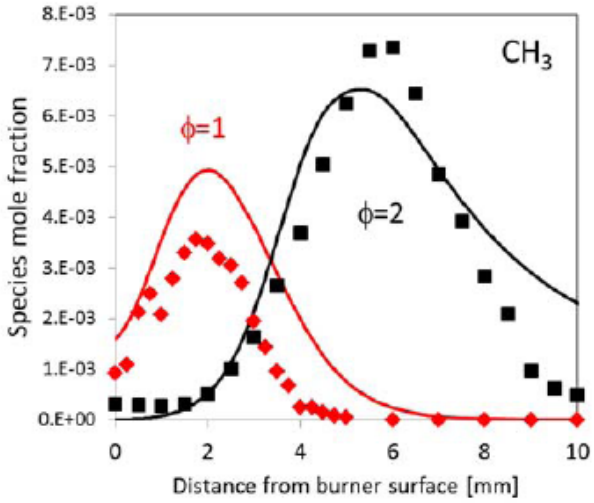


Low pressure MCH flame experiments (Skeen and Hansen, Sandia)



allyl radical





methyl radical

Pitz, Skeen, Hansen, and Mehl 2013 U.S. National Combustion Meeting

Technical accomplishments

Objective 4: Develop improved 2-component surrogate mechanism for diesel to be used for multidimensional CFD simulations.

Developing reduced model for diesel surrogate for Engine Combustion Network (ECN)

LLNL Detailed Mechanism
2885 species, 11754 reactions

~ 18 times reduction

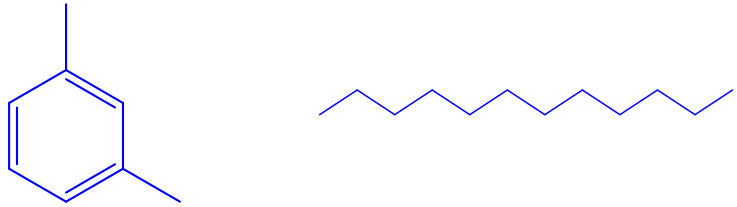
- DRG – X
- DRGASA
- Isomer Lumping
- DRG – X
- DRGASA

Skeletal Mechanism

163 species, 887 reactions

2-component diesel surrogate:

23% m-xylene / 77% n-dodecane
(by liquid volume)



Collaboration with Sibendu Som at ANL:

- Reduction of mechanism in collaboration with UCONN
- On-going work: extensive validation against ECN spray-combustion and engine data

DRG related algorithms developed by Prof. T. Lu at University of Connecticut

Mechanisms are available on LLNL website and by email

http://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion

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Science and Technology

home > science and technology > chemistry > combustion

Print View

- Hydrogen
- Ethanol
- Butanol isomers
- Iso-pentanol
- Dimethyl Ether
- CH4, C2H4, C2H6, C3H8, and nC4H10
- CH4, C2H4, C2H6, C3H6, C3H8, and NOx
- C8-C16 n-Alkanes
- Cyclohexane
- Methylcyclohexane
- Methyl Butanoate and Methyl Formate
- Methyl Decanoate
- Methyl Decenoates
- Biodiesel Surrogates
- Dimethyl Carbonate
- Heptane, Detailed Mechanism
- Heptane, Reduced Mechanism
- iso-Octane
- Gasoline Surrogate
- 2-Methyl Alkanes
- Primary Reference Fuels: iso-Octane / n-Heptane Mixtures
- 2,2,4,4,6,8,8-Heptamethylnonane

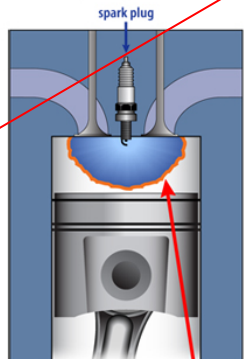
Combustion Chemistry

Go Directly to Mechanisms...

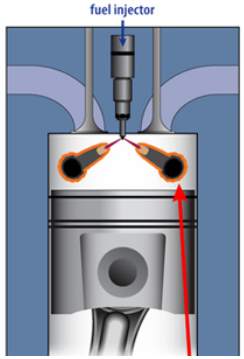
The central feature of the Combustion Chemistry project at LLNL is our development, validation, and application of detailed chemical kinetic reaction mechanisms for the combustion of hydrocarbon and other types of chemical fuels. For the past 30 years, our group has built hydrocarbon mechanisms for fuels from hydrogen and methane through much larger fuels including heptanes and octanes. Other classes of fuels for which models have been developed include flame suppressants such as halons and organophosphates, and air pollutants such as soot and oxides of nitrogen and sulfur.

Reaction mechanisms have been tested and validated extensively through comparisons between computed results and measured data from laboratory experiments (e.g., shock tubes, laminar flames, rapid compression machines, flow reactors, stirred reactors) and from practical systems (e.g., diesel engines, spark-ignition engines, homogeneous charge, compression ignition (HCCI) engines). We have used these kinetic models to examine a wide range of combustion systems.

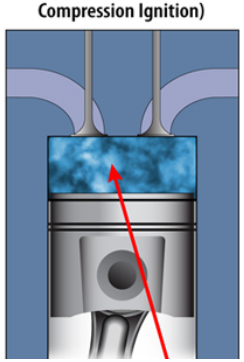
Gasoline Engine (Spark Ignition)



Diesel Engine (Compression Ignition)



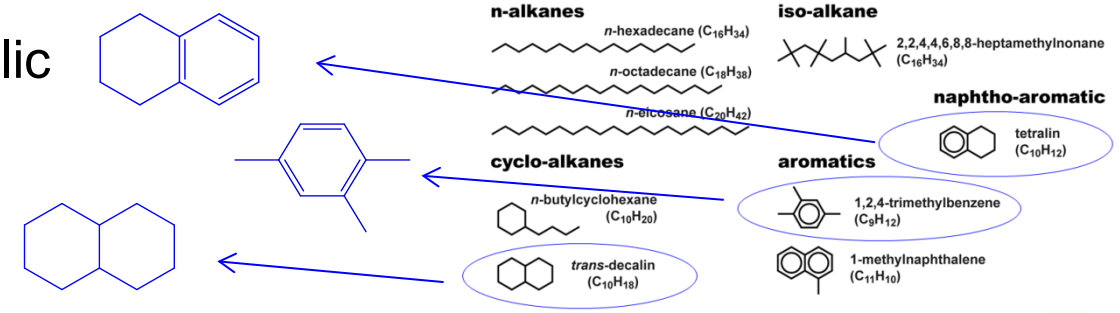
HCCI Engine (Homogeneous Charge Compression Ignition)



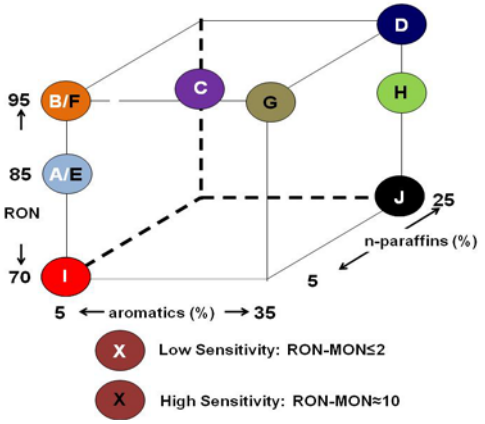
Gasoline Surrogate

Future plans for next year:

- Fill-out the 9 component surrogate palette for diesel (CRC AVFL-18 effort, “Surrogate fuels for kinetic modeling”)
  Develop mechanism for:
  - multi-ring saturated cyclic
  - larger alkyl aromatic
  - multi-ring cycloalkane



- Develop surrogates models for 5 of the FACE gasoline fuels
  - Validate surrogate models using experiments to be performed by KAUST, UC Berkeley, UCONN, and Rensselaer Polytechnic Institute

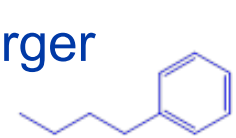


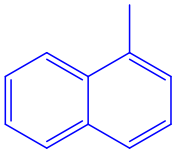
- Modeling of engine combustion with reduced models for diesel surrogate fuels for the Engine Combustion Network

Detailed chemical kinetic modeling summary

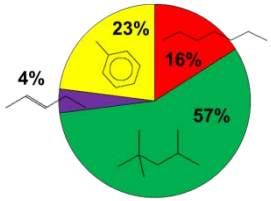
Developing fuel surrogate models for gasoline and diesel fuels to enable accurate engine simulations with fuel effects

1. Developed detailed chemical kinetic models for larger alkyl aromatics relevant to diesel fuels

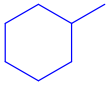


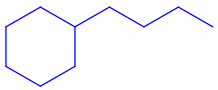


2. Developed surrogate kinetics models for gasoline-ethanol blends

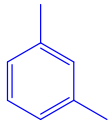


3. Developing improved chemical kinetic models for larger alkyl-cyclohexanes



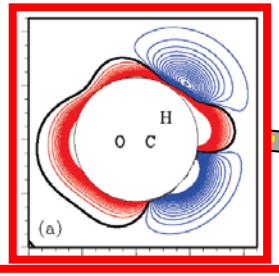


4. Developed an improved 2-component surrogate mechanism for diesel to be used for multidimensional CFD simulations



Technical Back-Up Slides

Chemical kinetic model development for practical fuels:



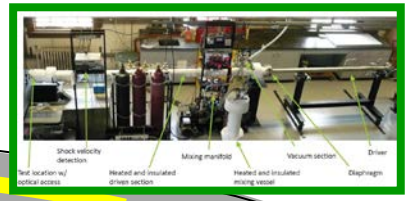
Ab initio calculations

Accurate reaction rates

Species thermodynamic properties

Reaction paths

Reaction rate rules



Detailed Chemical Kinetic Models

Fundamental Experiments

NUIG, UCONN, USC, CNRS, RPI

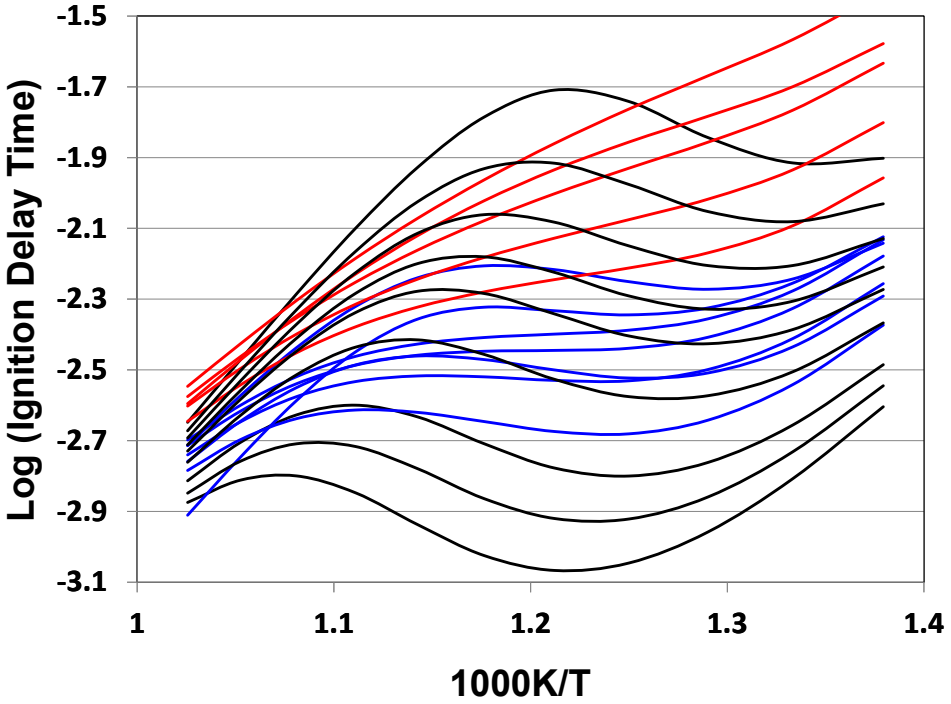
Model Reduction

Validation against fundamental combustion data

Application to engines

Gasoline surrogate formulation using model-derived correlations

Calculated ignition delay times can be correlated to octane characteristics of real fuels



PRFs (RON-MON=0)

Sensitive Fuels (0<RON-MON<10)

Highly Sensitive Fuels (RON-MON>11)

Correlations for gasoline surrogate formulation